Electron-deficient vanadium(III) alkyl and allyl complexes with amidinate ancillary ligands

Brussee, E.A C; Meetsma, A.; Hessen, B.; Teuben, J.H

Published in:
Organometallics

DOI:
10.1021/om980431e

Publication date:
1998

Supporting Material to:

Electron-Deficient Vanadium(III) Alkyl and Allyl Complexes with Amidinate Ancillary Ligands

Edward A. C. Brussee, Auke Meetsma, Bart Hessen, and Jan H. Teuben

Center for Catalytic Olefin Polymerization, Department of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

*Crystal Structure Data of [t-BuC(Ni-Pr)$_2$]VCl$_2$(THF)$_2$ (**5**), [PhC(NSiMe$_3$)$_2$]$_2$V(η^3-C$_3$H$_5$) (**8**), and[t-BuC(Ni-Pr)$_2$]V(η^3-C$_3$H$_5$)$_2$ (**11**)*

Crystal structure of [*t*-BuC(N*i*-Pr)$_2$]VCl$_2$(THF)$_2$ (5)

Suitable 'red-brown' needle plate-shaped crystals were obtained by slow diffusion of pentane in THF. The crystal, a parallelepiped of approximate size 0.25 x 0.34 x 0.50 mm., used for characterization and data collection was mounted on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen cold stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F* diffractometer[2], interfaced to a *INDY* (*Silicon Graphics*) *UNIX* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-K$\overline{\alpha}$ radiation, $\Delta\omega = 0.90 + 0.34$ tg θ).

Unit cell parameters[3] and orientation matrix were determined from a least-squares treatment of the *SET4*[4] setting angles of 22 reflections in the range $11.90° < \theta < 18.42°$. The unit cell was identified as monoclinic; reduced cell calculations did not indicate any higher metric lattice symmetry.[5] The space group $P2_1/n$ was derived from the systematic extinctions. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7]

The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. A 360° ψ-scan for a reflection close to axial (2-22) showed a variation in intensity of less than 13% about the mean value. Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and reduced to F_o^2.[8]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[9] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. The hydrogen atoms were included in the final refinement riding on their carrier atoms with $U = c \times U_{equiv}$ of their parent atom, where $c = 1.2$ for the

aromatic / non-methyl hydrogen atoms and c = 1.5 for the methyl hydrogen atoms and where values U_{equiv} are related to the atoms to which the H atoms are bonded. The methyl-groups were refined as rigid groups, which were allowed to rotate free. Some atoms showed large thermal displacement parameters suggesting some degree of disorder, which is in line with the weak scattering power of the crystals investigated.

Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.2108 for 4091 reflections with $F_o^2 \geq 0$ and $R(F)$ = 0.0803 for 2293 reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 243 parameters. The final difference Fourier map was essentially featureless with a few peaks of max. 1.13 e/Å^3 within the neighborhood of the tertiary butyl groups, which also showed large thermal displacement parameters.

The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum_h [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_0 and F_c are the observed and calculated structure factor amplitudes, respectively; a and b were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Crystal data and numerical details on data collection and refinement are given in Table 1, 2, and 3. Final fractional atomic coordinates equivalent displacement parameters for the non-hydrogen atoms are given in Table 4. Molecular geometry data are collected in Table 5, 6, and 7. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables of Crystallography.*[10] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[11] (least-square refinements), *PLATON*[12] (calculation of geometric data and the *ORTEP* illustrations, see Figure 1) and a locally modified version of the program *PLUTO*[13] (preparation of illustrations).

Crystal structure of [PhC(NSiMe$_3$)$_2$]$_2$V(η^3-C$_3$H$_5$) (8)

Suitable red colored block-shaped crystals were obtained by recrystallisation from pentane. The crystal, a parallelepiped of approximate size 0.25 x 0.30 x 0.45 mm., used for characterization and data collection was mounted on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen cold stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F* diffractometer[2] (Mo tube, 50 kV, 40 mA, monochromated Mo-K$\overline{\alpha}$ radiation, $\Delta\omega = 0.90 + 0.34$ tg θ), interfaced to a *MSDOS* computer.

Unit cell parameters[3] and orientation matrix were determined from a least-squares treatment of the *SET4*[4] setting angles of 22 reflections in the range $17.69° < \theta < 20.78°$. The unit cell

was identified as triclinic, space group $P\bar{1}$: the *E*-statistics statistics were indicative of a centrosymmetric space group.[4] Reduced cell calculations did not indicate any higher metric lattice symmetry[5] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7] The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. 360° ψ-scans for reflections close to axial showed a variation in intensity of less than 12% about the mean value. Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and reduced to F_o^2.[8]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[9] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. Refinement was complicated by a disorder problem: from the solution it was clear that the C28 atom position (of the allyl ligand) was disordered over two positions and so the whole ligand. In the final refinement the minor component of the disordered allyl ligand was restrained to the major component. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, except those belonging to the minor component of the allyl ligand. These hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using hybridization at the C-atom as appropriate with U_{iso} = 1.2 x U_{equiv} of their parent atom and at a multiplicity due to the disorder of the minor fraction. The s.o.f. of the major component of the disordered allyl ligand model refined to a value of 0.700(7). Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.0797 for 7374 reflections with $F_o^2 \geq 0$ and $R(F)$ = 0.0308 for 6601 reflection's with $F_o \geq 4.0\ \sigma(F_o)$ and 570 parameters. A final difference Fourier map did not show residual peaks outside the range ±0.40(5) e/Å^{-3}.

Final The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum_h [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_o and F_c are the observed and calculated structure factor amplitudes, respectively; *a* and *b* were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Crystal data and numerical details on data collection and refinement are given in Table 1, 2, and 3. Final fractional atomic coordinates equivalent displacement for the non-hydrogen atoms are given in Table 4. Molecular geometry data are collected in Table 5, 6, and 7. Neutral atom scattering factors and anomalous dispersion corrections were taken from

International Tables of Crystallography.[10] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[11] (least-square refinements), *PLATON*[12] (calculation of geometric data and the *ORTEP* illustrations, see Figure 2) and a locally modified version of the program *PLUTO*[13] (preparation of illustrations).

Crystal structure of [*t*-BuC(N*i*-Pr)$_2$]V(η^3-C$_3$H$_5$)$_2$ (11)

Suitable red-brown colored block-shaped crystals were obtained by recrystallisation from pentane. The crystal, a parallelepiped of approximate size 0.12 x 0.20 x 0.44 mm., used for characterization and data collection was mounted on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen cold stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F* diffractometer[2], interfaced to a *INDY* (*Silicon Graphics*) *UNIX* computer (Mo tube, 50 kV, 40 mA; monochromated Mo-K$\overline{\alpha}$ radiation, $\Delta\omega = 0.90 + 0.34$ tg θ).

Cell constants and orientation matrices[3] for data collection were obtained from systematic searches of limited hemispheres of reciprocal space; sets of diffraction maxima were located whose *SET4*[4] setting angles (22 reflections in the range $12.22° < \theta < 18.21°$) were refined by least squares. The unit cell was identified as monoclinic; reduced cell calculations did not indicate any higher metric lattice symmetry.[6] The space group *C*2/*c* was determined from considerations of the unit cell parameters, statistical analyses of intensity distributions and where appropriate systematic absences. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7]

The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. A 360° ψ-scan for a reflections close to axial (-200) showed variation in intensity of less than 13% about the mean value. Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and reduced to F_o^2.[8]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[9] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic thermal displacement parameters were refined.

Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2) = 0.930$ or 3587 reflections with $F_o^2 \geq 0$ and $R(F) = 0.0401$ for 2649 reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 313 parameters. The final difference Fourier map was essentially

featureless: no significant peaks (0.56(5) e/Å^3) having chemical meaning above the general background were observed.

The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum_h [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_0 and F_c are the observed and calculated structure factor amplitudes, respectively; a and b were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Crystal data and numerical details on data collection and refinement are given in Table 1, 2, and 3. Final fractional atomic coordinates equivalent displacement parameters for the non-hydrogen atoms are given in Table 4. Molecular geometry data are collected in Table 5, 6, and 7. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables of Crystallography.*[10] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[11] (least-square refinements), *PLATON*[12] (calculation of geometric data and the *ORTEP* illustrations, see Figure 3) and a locally modified version of the program *PLUTO*[13] (preparation of illustrations).

Table 1. Crystal data and details of the structure determination.

Compound	**5**	**8**	**11**
Formula	$C_{19}H_{39}Cl_3N_2O_2V$	$C_{29}H_{51}N_4Si_4V$	$C_{17}H_{33}N_2V$
fw, g.mol^{-1}	449.38	619.03	316.40
Crystal system	monoclinic	triclinic	monoclinic
Space group, no.[19]	$P2_1/n$, 14	$P\bar{1}$, 2	$C2/c$, 15
a, Å	12.593(1)	10.900(1)	12.800(1)
b, Å	12.216(1)	11.849(1)	16.380(1)
c, Å	14.945(1)	15.208(1)	18.531(1)
α, deg		112.598(4)	
β, deg	92.85(1)	99.134(5)	109.331(7)
γ, deg		93.208(4)	
V, Å^3	2296.2(3)	1775.3(3)	3666.2(4)
Z	4	2	8
ρ_{calc}, g.cm^{-3}	1.300	1.158	1.146
F(000), electrons	960	664	1376
μ(Mo K$\bar{\alpha}$), cm^{-1}	6.8	4.4	5.4
color, habit	'red-brown', needle	red, block-shaped	red-brown, parrellepiped
Approx. crystal dimension, mm	0.25 x 0.34 x 0.50	0.25 x 0.30 x 0.45	0.12 x 0.20 x 0.44

Table 2. Data collection.

Compound	5	8	11
Radiation	Mo $K\overline{\alpha}$	Mo $K\overline{\alpha}$	Mo $K\overline{\alpha}$
Wavelength, Å	0.71073	0.71073	0.71073
Monochromator	Graphite	Graphite	Graphite
Temperature, K	130	130	130
θ range; min. max., deg	1.36, 27.0	1.40, 27.0	1.17, 26.0
ω/2θ scan, deg	$\Delta\omega = 0.90 + 0.34\ tg\theta$	$\Delta\omega = 0.90 + 0.34\ tg\theta$	$\Delta\omega = 0.90 + 0.34\ tg\theta$
Index ranges	h: 0→14 k: 0→14 l: -19→17	h: -13→13 k: -15→13 l: 0→19	h: -15→0 k: 0→20 l: -21→22
Crystal-to-receiving-aperture-distance, mm	173	173	173
Horizontal-, vertical-aperture, mm	3.2 + tg θ; 4.0	3.2 + tg θ; 4.0	3.2 + tg θ; 4.0
Reference reflections, r.m.s. dev. in %	222, 2.85 2-20-7, 1.43 2-22, 1.44	-1-14, 0.8 021, 1.0 400, 0.7	-2-20, 3.3 -3-1-2, 2.5 -2-21, 1.8
Drift correction	1.000 - 1.040	1.000 - 1.009	1.000 - 1.007
X-ray exposure time, h	107.8	107.36	76.9
Total data	4516	7990	3894
Unique data	4091	7694	3587
Data with criterion: ($F_o \geq 4.0\ \sigma(F_o)$)	2293	6601	2649
$R_{int} = \sum [\lvert F_o^2 - F_o^2\ (mean)\rvert] / \sum [F_o^2]$	0.046	0.010	0.0302
$R_{sig} = \sum \sigma(F_o^2) / \sum [F_o^2]$	0.105	0.018	0.0354

Table 3. Refinement.

Compound	5	8	11
Number of reflections ($F_o^2 \geq 0$)	4091	7347	3587
Number of refined parameters	243	570	313
Final agreement factors: $wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ for $F_o^2 > 0$	0.2108	0.0797	0.0930
Weighting scheme: *a, b* $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2] / 3$	0.0977, 2.00	0.0486, 0.519	0.0530, 0.0
$R(F) = \sum (\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert) / \sum\lvert F_o\rvert$ for $F_o > 4.0\ \sigma(F_o)$	0.0803	0.0308	0.0401
GooF = S = $[\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ n = number of reflections; p = number of parameters refined	1.047	1.032	0.995
Residual electron density in final difference Fourier map, e/Å^3	-0.54, 1.13(12)	-0.37, 0.40(5)	-0.25, 0.56(5)
Max. (shift/σ) final cycle	< 0.001	< 0.001	< 0.001

Table 4. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
[*t*-BuC(N*i*-Pr)$_2$]VCl$_2$(THF)$_2$ (**5**)				
V(1)	0.46747(9)	0.73111(9)	0.28976(7)	0.0159(3)
Cl(1)	0.28018(13)	0.72229(16)	0.30993(11)	0.0278(5)
Cl(2)	0.51399(14)	0.71847(15)	0.4457(1)	0.0270(5)
O(1)	0.4725(4)	0.5629(3)	0.2841(3)	0.0255(16)
O(2)	0.4551(4)	0.8984(3)	0.2999(3)	0.0227(16)
N(1)	0.4730(4)	0.7398(4)	0.1543(3)	0.0177(17)
N(2)	0.6140(4)	0.7473(4)	0.2399(3)	0.0202(17)
C(1)	0.3926(5)	0.7313(7)	0.0785(4)	0.029(2)
C(2)	0.3348(8)	0.6210(8)	0.0872(6)	0.055(4)
C(3)	0.3176(7)	0.8281(8)	0.0825(6)	0.050(3)
C(4)	0.5775(5)	0.7512(5)	0.1541(4)	0.018(2)
C(5)	0.6415(5)	0.7647(6)	0.0680(4)	0.024(2)
C(6)	0.6325(9)	0.6563(8)	0.0165(6)	0.068(4)
C(7)	0.5976(8)	0.8584(9)	0.0123(6)	0.064(4)
C(8)	0.7583(8)	0.7858(11)	0.0810(6)	0.073(4)
C(9)	0.7207(5)	0.7610(6)	0.2810(5)	0.030(2)
C(10)	0.7548(7)	0.6560(7)	0.3300(6)	0.045(3)
C(11)	0.7257(7)	0.8568(7)	0.3446(5)	0.039(3)
C(12)	0.5345(7)	0.4969(5)	0.2266(5)	0.032(3)
C(13)	0.4867(6)	0.3844(6)	0.2310(5)	0.035(3)
C(14)	0.4532(7)	0.3771(6)	0.3256(5)	0.033(3)
C(15)	0.4164(8)	0.4905(6)	0.3461(6)	0.046(3)
C(16)	0.4006(7)	0.9533(6)	0.3714(6)	0.037(3)
C(17)	0.4559(9)	1.0612(7)	0.3784(6)	0.056(4)
C(18)	0.4846(7)	1.0881(6)	0.2866(6)	0.046(3)
C(19)	0.4900(7)	0.9815(6)	0.2377(6)	0.039(3)
[PhC(NSiMe$_3$)$_2$]$_2$V(η^3-C$_3$H$_5$) (**8**)				
V	0.28585(2)	0.05525(2)	0.30991(2)	0.0161(1)
Si(1)	0.43754(4)	0.25417(4)	0.22506(3)	0.0216(1)
Si(2)	0.07299(4)	0.25726(4)	0.44157(3)	0.0207(1)
Si(3)	0.52183(4)	-0.15137(4)	0.21781(3)	0.0229(1)
Si(4)	0.01074(4)	-0.12264(4)	0.14863(3)	0.0234(1)
N(1)	0.32382(11)	0.20251(11)	0.27476(9)	0.0195(3)
N(2)	0.17428(11)	0.20163(11)	0.36093(9)	0.0187(3)
N(3)	0.37902(11)	-0.09134(11)	0.22201(9)	0.0199(3)
N(4)	0.17137(12)	-0.08214(12)	0.19307(9)	0.0219(3)
C(1)	0.4709(2)	0.11629(17)	0.12548(14)	0.0349(6)
C(2)	0.57892(19)	0.3275(2)	0.32295(15)	0.0440(6)
C(3)	0.3919(2)	0.36691(17)	0.17193(14)	0.0338(6)
C(4)	0.23602(13)	0.26114(13)	0.32033(10)	0.0179(4)
C(5)	0.21104(14)	0.38535(13)	0.32322(11)	0.0200(4)
C(6)	0.27959(15)	0.49207(15)	0.39522(12)	0.0254(4)
C(7)	0.25865(18)	0.60620(15)	0.39489(13)	0.0329(5)
C(8)	0.16892(18)	0.61410(16)	0.32303(14)	0.0339(5)
C(9)	0.09984(17)	0.50818(16)	0.25175(14)	0.0327(5)
C(10)	0.12027(15)	0.39406(15)	0.25174(12)	0.0262(5)
C(11)	0.16502(19)	0.3603(2)	0.56366(13)	0.0356(6)
C(12)	-0.04893(18)	0.3402(2)	0.40117(15)	0.0353(6)

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
C(13)	-0.0091(2)	0.12289(19)	0.45222(17)	0.0400(6)
C(14)	0.5235(2)	-0.2718(2)	0.26803(16)	0.0394(7)
C(15)	0.55993(19)	-0.2191(2)	0.09419(13)	0.0370(6)
C(16)	0.64877(17)	-0.0238(2)	0.29554(15)	0.0365(6)
C(17)	0.26929(14)	-0.13992(13)	0.16446(10)	0.0199(4)
C(18)	0.25434(14)	-0.25108(14)	0.07091(11)	0.0237(4)
C(19)	0.25385(17)	-0.23610(18)	-0.01534(12)	0.0326(5)
C(20)	0.24325(19)	-0.3384(2)	-0.10161(14)	0.0451(7)
C(21)	0.2337(2)	-0.4547(2)	-0.10242(16)	0.0518(7)
C(22)	0.2330(2)	-0.47037(18)	-0.01767(17)	0.0491(7)
C(23)	0.24315(18)	-0.36867(16)	0.06931(14)	0.0359(6)
C(24)	-0.06025(18)	0.02096(18)	0.16387(16)	0.0355(6)
C(25)	-0.05281(17)	-0.20203(18)	0.21929(16)	0.0339(6)
C(26)	-0.0370(2)	-0.2260(2)	0.01743(15)	0.0463(7)
C(27)[a]	0.4334(13)	0.1320(11)	0.4498(13)	0.030(2)
C(28)[a]	0.3320(3)	0.0737(3)	0.46764(18)	0.0294(9)
C(29)[a]	0.2806(6)	-0.0469(5)	0.4137(5)	0.0271(13)
C(30)[b]	0.434(3)	0.158(2)	0.455(3)	0.026(4)
C(31)[b]	0.3972(6)	0.0362(6)	0.4407(4)	0.0256(18)
C(32)[b]	0.2757(16)	-0.0083(11)	0.4300(12)	0.033(4)
[*t*-BuC(N*i*-Pr)$_2$]V(η^3-C$_3$H$_5$)$_2$ (**11**)				
V(1)	0.21441(3)	0.06627(2)	0.16961(2)	0.0213(1)
N(1)	0.27580(14)	0.03696(11)	0.08095(10)	0.0221(5)
N(2)	0.23889(15)	-0.05334(10)	0.15622(10)	0.0239(6)
C(1)	0.32356(18)	0.07982(13)	0.03005(13)	0.0262(7)
C(2)	0.3862(2)	0.15589(15)	0.06769(16)	0.0341(8)
C(3)	0.2313(2)	0.10168(17)	-0.04329(14)	0.0355(8)
C(4)	0.29254(16)	-0.03921(12)	0.10530(12)	0.0203(6)
C(5)	0.37269(19)	-0.09896(14)	0.08496(14)	0.0308(7)
C(6)	0.4899(2)	-0.06313(19)	0.11651(18)	0.0418(9)
C(7)	0.3359(3)	-0.11260(19)	-0.00196(17)	0.0457(10)
C(8)	0.3810(3)	-0.18365(18)	0.1218(2)	0.0518(13)
C(9)	0.1873(2)	-0.13026(13)	0.16639(14)	0.0325(8)
C(10)	0.0996(3)	-0.15586(19)	0.0928(2)	0.0488(10)
C(11)	0.1382(4)	-0.1230(2)	0.2297(2)	0.0584(15)
C(12)	0.1333(2)	0.19058(16)	0.11924(19)	0.0421(10)
C(13)	0.0604(2)	0.14367(17)	0.14192(18)	0.0457(10)
C(14)	0.0306(2)	0.06499(19)	0.1147(2)	0.050(1)
C(15)	0.3561(2)	0.13166(18)	0.24791(16)	0.0410(9)
C(16)	0.2781(3)	0.13166(18)	0.28438(15)	0.0446(9)
C(17)	0.2286(3)	0.0622(2)	0.29874(15)	0.0461(10)

*) $U_{eq} = 1/3\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ [20]
[a] Indicates an s.o.f. of 0.700(7)
[b] Indicates an s.o.f. of 0.300(7)

Table 5. Selected Interatomic Distances (Å)
Standard deviations in the last decimal place are given in parentheses.

[*t*-BuC(N*i*-Pr)$_2$]VCl$_2$(THF)$_2$ (**5**)					
V(1)-Cl(1)	2.395(2)	N(1)-C(1)	1.485(8)	C(9)-C(10)	1.528(11)
V(1)-Cl(2)	2.3796(18)	N(1)-C(4)	1.323(8)	C(9)-C(11)	1.507(11)
V(1)-O(1)	2.058(4)	N(2)-C(4)	1.341(8)	C(12)-C(13)	1.503(10)
V(1)-O(2)	2.056(4)	N(2)-C(9)	1.459(8)	C(13)-C(14)	1.498(11)
V(1)-N(1)	2.032(5)	C(1)-C(2)	1.540(13)	C(14)-C(15)	1.497(11)
V(1)-N(2)	2.034(5)	C(1)-C(3)	1.516(12)	C(16)-C(17)	1.492(12)
O(1)-C(12)	1.437(9)	C(4)-C(5)	1.561(9)	C(17)-C(18)	1.473(13)
O(1)-C(15)	1.485(10)	C(5)-C(6)	1.533(12)	C(18)-C(19)	1.496(11)
O(2)-C(16)	1.461(10)	C(5)-C(7)	1.504(12)		
O(2)-C(19)	1.459(9)	C(5)-C(8)	1.496(12)		
[PhC(NSiMe$_3$)$_2$]$_2$V(η^3-C$_3$H$_5$) (**8**)					
V-N(1)	2.0509(14)	Si(2)-C(12)	1.861(2)	C(5)-C(10)	1.388(2)
V-N(2)	2.1438(13)	Si(2)-C(13)	1.856(2)	C(6)-C(7)	1.386(3)
V-N(3)	2.1642(13)	Si(3)-N(3)	1.7483(13)	C(7)-C(8)	1.382(3)
V-N(4)	2.0507(14)	Si(3)-C(14)	1.859(3)	C(8)-C(9)	1.380(3)
V-C(27)	2.280(17)	Si(3)-C(15)	1.8648(19)	C(9)-C(10)	1.383(3)
V-C(28)	2.293(3)	Si(3)-C(16)	1.861(2)	C(17)-C(18)	1.499(2)
V-C(29)	2.334(7)	Si(4)-N(4)	1.7411(14)	C(18)-C(19)	1.389(2)
V-C(30)	2.35(4)	Si(4)-C(24)	1.858(2)	C(18)-C(23)	1.382(3)
V-C(31)	2.256(6)	Si(4)-C(25)	1.860(2)	C(19)-C(20)	1.385(3)
V-C(32)	2.242(16)	Si(4)-C(26)	1.863(2)	C(20)-C(21)	1.371(4)
Si(1)-N(1)	1.7460(14)	N(1)-C(4)	1.3399(19)	C(21)-C(22)	1.372(3)
Si(1)-C(1)	1.854(2)	N(2)-C(4)	1.320(2)	C(22)-C(23)	1.388(3)
Si(1)-C(2)	1.863(2)	N(3)-C(17)	1.3151(19)	C(27)-C(28)	1.387(15)
Si(1)-C(3)	1.861(2)	N(4)-C(17)	1.341(2)	C(28)-C(29)	1.375(8)
Si(2)-N(2)	1.7462(13)	C(4)-C(5)	1.497(2)	C(30)-C(31)	1.40(3)
Si(2)-C(11)	1.8630(19)	C(5)-C(6)	1.387(2)	C(31)-C(32)	1.358(19)
[*t*-BuC(N*i*-Pr)$_2$]V(η^3-C$_3$H$_5$)$_2$ (**11**)					
V(1)-N(1)	2.0981(19)	N(1)-C(1)	1.462(3)	C(5)-C(7)	1.538(4)
V(1)-N(2)	2.0124(17)	N(1)-C(4)	1.320(3)	C(5)-C(8)	1.534(4)
V(1)-C(12)	2.335(3)	N(2)-C(4)	1.358(3)	C(9)-C(10)	1.511(4)
V(1)-C(13)	2.255(3)	N(2)-C(9)	1.463(3)	C(9)-C(11)	1.508(5)
V(1)-C(14)	2.233(3)	C(1)-C(2)	1.520(3)	C(12)-C(13)	1.377(4)
V(1)-C(15)	2.191(3)	C(1)-C(3)	1.519(3)	C(13)-C(14)	1.391(4)
V(1)-C(16)	2.278(3)	C(4)-C(5)	1.552(3)	C(15)-C(16)	1.378(5)
V(1)-C(17)	2.340(3)	C(5)-C(6)	1.535(4)	C(16)-C(17)	1.371(5)

Table 6. Selected Bond angles (deg.)
Standard deviations in the last decimal place are given in parentheses.

[*t*-BuC(N*i*-Pr)$_2$]VCl$_2$(THF)$_2$ (**5**)			
Cl(1)-V(1)-Cl(2)	94.00(7)	V(1)-N(2)-C(9)	133.7(4)
Cl(1)-V(1)-O(1)	89.59(15)	C(4)-N(2)-C(9)	131.5(5)
Cl(1)-V(1)-O(2)	87.52(15)	N(1)-C(1)-C(2)	107.7(6)
Cl(1)-V(1)-N(1)	102.15(15)	N(1)-C(1)-C(3)	108.5(6)
Cl(1)-V(1)-N(2)	165.38(15)	C(2)-C(1)-C(3)	112.4(6)
Cl(2)-V(1)-O(1)	88.22(14)	N(1)-C(4)-N(2)	106.7(5)
Cl(2)-V(1)-O(2)	90.47(14)	N(1)-C(4)-C(5)	124.6(5)
Cl(2)-V(1)-N(1)	163.78(16)	N(2)-C(4)-C(5)	128.7(5)

Cl(2)-V(1)-N(2)	100.46(14)	C(4)-C(5)-C(6)	107.1(6)
O(1)-V(1)-O(2)	176.7(2)	C(4)-C(5)-C(7)	110.2(6)
O(1)-V(1)-N(1)	90.49(19)	C(4)-C(5)-C(8)	117.1(6)
O(1)-V(1)-N(2)	93.0(2)	C(6)-C(5)-C(7)	111.3(6)
O(2)-V(1)-N(1)	91.60(19)	C(6)-C(5)-C(8)	105.2(8)
O(2)-V(1)-N(2)	90.2(2)	C(7)-C(5)-C(8)	105.8(7)
N(1)-V(1)-N(2)	63.46(19)	N(2)-C(9)-C(10)	109.7(6)
V(1)-O(1)-C(12)	127.1(4)	N(2)-C(9)-C(11)	111.3(6)
V(1)-O(1)-C(15)	123.5(4)	C(10)-C(9)-C(11)	110.3(6)
C(12)-O(1)-C(15)	109.2(5)	O(1)-C(12)-C(13)	104.8(6)
V(1)-O(2)-C(16)	123.4(4)	C(12)-C(13)-C(14)	103.2(6)
V(1)-O(2)-C(19)	128.2(4)	C(13)-C(14)-C(15)	104.0(6)
C(16)-O(2)-C(19)	108.3(5)	O(1)-C(15)-C(14)	105.2(7)
V(1)-N(1)-C(1)	134.5(4)	O(2)-C(16)-C(17)	102.8(7)
V(1)-N(1)-C(4)	95.2(4)	C(16)-C(17)-C(18)	105.5(7)
C(1)-N(1)-C(4)	130.2(5)	C(17)-C(18)-C(19)	106.3(7)
V(1)-N(2)-C(4)	94.6(4)	O(2)-C(19)-C(18)	105.8(7)

$[PhC(NSiMe_3)_2]_2V(\eta^3\text{-}C_3H_5)$ (**8**)

N(1)-V-N(2)	64.82(5)	N(3)-Si(3)-C(15)	114.67(8)
N(1)-V-N(3)	106.26(5)	N(3)-Si(3)-C(16)	108.02(8)
N(1)-V-N(4)	109.10(5)	C(14)-Si(3)-C(15)	108.30(11)
N(1)-V-C(27)	93.8(4)	C(14)-Si(3)-C(16)	108.26(10)
N(1)-V-C(28)	121.07(10)	C(15)-Si(3)-C(16)	107.46(9)
N(1)-V-C(29)	155.62(17)	N(4)-Si(4)-C(24)	107.95(8)
N(1)-V-C(30)	87.8(8)	N(4)-Si(4)-C(25)	108.05(8)
N(1)-V-C(31)	122.38(19)	N(4)-Si(4)-C(26)	115.84(8)
N(1)-V-C(32)	146.1(4)	C(24)-Si(4)-C(25)	111.23(10)
N(2)-V-N(3)	164.97(5)	C(24)-Si(4)-C(26)	106.09(10)
N(2)-V-N(4)	105.76(5)	C(25)-Si(4)-C(26)	107.72(10)
N(2)-V-C(27)	93.5(4)	V-N(1)-Si(1)	137.36(8)
N(2)-V-C(28)	86.14(9)	V-N(1)-C(4)	91.58(10)
N(2)-V-C(29)	104.62(17)	Si(1)-N(1)-C(4)	130.29(12)
N(2)-V-C(30)	88.0(8)	V-N(2)-Si(2)	142.04(8)
N(2)-V-C(31)	107.87(17)	V-N(2)-C(4)	88.12(9)
N(2)-V-C(32)	95.0(4)	Si(2)-N(2)-C(4)	128.37(12)
N(3)-V-N(4)	64.57(5)	V-N(3)-Si(3)	143.22(7)
N(3)-V-C(27)	99.3(4)	V-N(3)-C(17)	87.53(9)
N(3)-V-C(28)	108.87(9)	Si(3)-N(3)-C(17)	128.88(11)
N(3)-V-C(29)	88.14(17)	V-N(4)-Si(4)	136.54(8)
N(3)-V-C(30)	104.2(8)	V-N(4)-C(17)	91.70(9)
N(3)-V-C(31)	87.09(17)	Si(4)-N(4)-C(17)	131.58(11)
N(3)-V-C(32)	98.3(4)	N(1)-C(4)-N(2)	115.48(15)
N(4)-V-C(27)	154.7(4)	N(1)-C(4)-C(5)	121.15(14)
N(4)-V-C(28)	128.34(10)	N(2)-C(4)-C(5)	123.37(13)
N(4)-V-C(29)	94.76(17)	C(4)-C(5)-C(6)	120.82(14)
N(4)-V-C(30)	161.5(7)	C(4)-C(5)-C(10)	119.74(14)
N(4)-V-C(31)	126.59(19)	C(6)-C(5)-C(10)	119.42(16)
N(4)-V-C(32)	102.4(4)	C(5)-C(6)-C(7)	120.17(16)
C(27)-V-C(28)	35.3(4)	C(6)-C(7)-C(8)	120.08(17)
C(27)-V-C(29)	64.0(4)	C(7)-C(8)-C(9)	119.90(19)
C(28)-V-C(29)	34.56(19)	C(8)-C(9)-C(10)	120.28(18)
C(30)-V-C(31)	35.2(8)	C(5)-C(10)-C(9)	120.14(16)
C(30)-V-C(32)	63.4(9)	N(3)-C(17)-N(4)	116.03(13)
C(31)-V-C(32)	35.1(5)	N(3)-C(17)-C(18)	122.26(14)

N(1)-Si(1)-C(1)	106.55(8)	N(4)-C(17)-C(18)	121.68(13)
N(1)-Si(1)-C(2)	107.82(8)	C(17)-C(18)-C(19)	119.73(16)
N(1)-Si(1)-C(3)	115.75(8)	C(17)-C(18)-C(23)	120.94(15)
C(1)-Si(1)-C(2)	111.45(10)	C(19)-C(18)-C(23)	119.32(16)
C(1)-Si(1)-C(3)	107.14(9)	C(18)-C(19)-C(20)	120.0(2)
C(2)-Si(1)-C(3)	108.17(10)	C(19)-C(20)-C(21)	120.4(2)
N(2)-Si(2)-C(11)	109.73(8)	C(20)-C(21)-C(22)	120.0(2)
N(2)-Si(2)-C(12)	113.91(8)	C(21)-C(22)-C(23)	120.2(2)
N(2)-Si(2)-C(13)	107.64(9)	C(18)-C(23)-C(22)	120.09(18)
C(11)-Si(2)-C(12)	109.56(10)	V-C(27)-C(28)	72.8(7)
C(11)-Si(2)-C(13)	108.36(10)	V-C(28)-C(27)	71.9(7)
C(12)-Si(2)-C(13)	107.46(10)	V-C(28)-C(29)	74.4(3)
N(3)-Si(3)-C(14)	109.92(9)	C(27)-C(28)-C(29)	124.6(8)
V-C(29)-C(28)	71.1(3)	V-C(31)-C(32)	71.9(7)
V-C(30)-C(31)	68.6(15)	C(30)-C(31)-C(32)	122.3(16)
V-C(31)-C(30)	76.2(16)	V-C(32)-C(31)	73.0(7)

[*t*-BuC(N*i*-Pr)$_2$]V(η^3-C$_3$H$_5$)$_2$ (**11**)

N(1)-V(1)-N(2)	64.32(7)	C(1)-N(1)-C(4)	128.25(19)
N(1)-V(1)-C(12)	96.82(9)	V(1)-N(2)-C(4)	93.15(12)
N(1)-V(1)-C(13)	118.44(9)	V(1)-N(2)-C(9)	136.64(16)
N(1)-V(1)-C(14)	104.61(10)	C(4)-N(2)-C(9)	126.14(18)
N(1)-V(1)-C(15)	100.83(9)	N(1)-C(1)-C(2)	111.54(19)
N(1)-V(1)-C(16)	136.70(11)	N(1)-C(1)-C(3)	108.9(2)
N(1)-V(1)-C(17)	150.67(11)	C(2)-C(1)-C(3)	110.7(2)
N(2)-V(1)-C(12)	150.04(9)	N(1)-C(4)-N(2)	109.66(18)
N(2)-V(1)-C(13)	132.78(9)	N(1)-C(4)-C(5)	123.96(19)
N(2)-V(1)-C(14)	96.79(10)	N(2)-C(4)-C(5)	126.03(18)
N(2)-V(1)-C(15)	115.41(10)	C(4)-C(5)-C(6)	107.9(2)
N(2)-V(1)-C(16)	123.42(9)	C(4)-C(5)-C(7)	110.4(2)
N(2)-V(1)-C(17)	97.81(10)	C(4)-C(5)-C(8)	114.6(2)
C(12)-V(1)-C(13)	34.87(10)	C(6)-C(5)-C(7)	112.1(2)
C(12)-V(1)-C(14)	64.16(11)	C(6)-C(5)-C(8)	105.1(2)
C(12)-V(1)-C(15)	89.97(11)	C(7)-C(5)-C(8)	106.7(2)
C(12)-V(1)-C(16)	86.42(11)	N(2)-C(9)-C(10)	110.8(2)
C(12)-V(1)-C(17)	107.90(12)	N(2)-C(9)-C(11)	110.8(2)
C(13)-V(1)-C(14)	36.09(11)	C(10)-C(9)-C(11)	110.3(3)
C(13)-V(1)-C(15)	110.21(11)	V(1)-C(12)-C(13)	69.40(16)
C(13)-V(1)-C(16)	87.93(12)	V(1)-C(13)-C(12)	75.74(17)
C(13)-V(1)-C(17)	90.85(12)	V(1)-C(13)-C(14)	71.08(17)
C(14)-V(1)-C(15)	145.36(11)	C(12)-C(13)-C(14)	122.6(3)
C(14)-V(1)-C(16)	115.30(13)	V(1)-C(14)-C(13)	72.83(17)
C(14)-V(1)-C(17)	100.32(13)	V(1)-C(15)-C(16)	75.50(17)
C(15)-V(1)-C(16)	35.87(12)	V(1)-C(16)-C(15)	68.63(16)
C(15)-V(1)-C(17)	64.51(12)	V(1)-C(16)-C(17)	75.25(17)
C(16)-V(1)-C(17)	34.50(12)	C(15)-C(16)-C(17)	123.5(3)
V(1)-N(1)-C(1)	137.75(14)	V(1)-C(17)-C(16)	70.26(16)
V(1)-N(1)-C(4)	90.52(13)		

Table 7. Selected Torsion angles (deg.)
Standard deviations in the last decimal place are given in parentheses.

[*t*-BuC(N*i*-Pr)$_2$]VCl$_2$(THF)$_2$ (**5**)			
Cl(1)-V(1)-O(1)-C(12)	141.3(5)	V(1)-O(1)-C(15)-C(14)	-172.9(5)
Cl(1)-V(1)-O(1)-C(15)	-43.6(5)	C(12)-O(1)-C(15)-C(14)	3.0(8)
Cl(2)-V(1)-O(1)-C(12)	-124.7(5)	V(1)-O(2)-C(16)-C(17)	152.8(5)
Cl(2)-V(1)-O(1)-C(15)	50.4(5)	C(19)-O(2)-C(16)-C(17)	-30.9(8)
N(1)-V(1)-O(1)-C(12)	39.1(6)	V(1)-O(2)-C(19)-C(18)	-167.5(5)
N(1)-V(1)-O(1)-C(15)	-145.8(6)	C(16)-O(2)-C(19)-C(18)	16.5(8)
N(2)-V(1)-O(1)-C(12)	-24.3(6)	V(1)-N(1)-C(1)-C(2)	-55.8(8)
N(2)-V(1)-O(1)-C(15)	150.8(6)	V(1)-N(1)-C(1)-C(3)	66.2(8)
Cl(1)-V(1)-O(2)-C(16)	48.9(5)	C(4)-N(1)-C(1)-C(2)	120.6(7)
Cl(1)-V(1)-O(2)-C(19)	-126.6(6)	C(4)-N(1)-C(1)-C(3)	-117.5(7)
Cl(2)-V(1)-O(2)-C(16)	-45.1(5)	V(1)-N(1)-C(4)-N(2)	1.5(5)
Cl(2)-V(1)-O(2)-C(19)	139.4(6)	V(1)-N(1)-C(4)-C(5)	-179.3(5)
N(1)-V(1)-O(2)-C(16)	151.0(5)	C(1)-N(1)-C(4)-N(2)	-175.9(6)
N(1)-V(1)-O(2)-C(19)	-24.5(6)	C(1)-N(1)-C(4)-C(5)	3.4(10)
N(2)-V(1)-O(2)-C(16)	-145.6(5)	V(1)-N(2)-C(4)-N(1)	-1.5(5)
N(2)-V(1)-O(2)-C(19)	39.0(6)	V(1)-N(2)-C(4)-C(5)	179.3(6)
Cl(1)-V(1)-N(1)-C(1)	-6.6(6)	C(9)-N(2)-C(4)-N(1)	-176.3(6)
Cl(1)-V(1)-N(1)-C(4)	176.2(3)	C(9)-N(2)-C(4)-C(5)	4.5(11)
O(1)-V(1)-N(1)-C(1)	83.1(6)	V(1)-N(2)-C(9)-C(10)	68.4(8)
O(1)-V(1)-N(1)-C(4)	-94.1(4)	V(1)-N(2)-C(9)-C(11)	-54.0(8)
O(2)-V(1)-N(1)-C(1)	-94.4(6)	C(4)-N(2)-C(9)-C(10)	-118.8(7)
O(2)-V(1)-N(1)-C(4)	88.4(4)	C(4)-N(2)-C(9)-C(11)	118.8(7)
N(2)-V(1)-N(1)-C(1)	176.1(7)	N(1)-C(4)-C(5)-C(6)	-67.2(8)
N(2)-V(1)-N(1)-C(4)	-1.1(3)	N(1)-C(4)-C(5)-C(7)	54.1(9)
Cl(2)-V(1)-N(2)-C(4)	178.8(3)	N(1)-C(4)-C(5)-C(8)	175.1(8)
Cl(2)-V(1)-N(2)-C(9)	-6.6(6)	N(2)-C(4)-C(5)-C(6)	111.9(8)
O(1)-V(1)-N(2)-C(4)	90.1(4)	N(2)-C(4)-C(5)-C(7)	-126.8(7)
O(1)-V(1)-N(2)-C(9)	-95.3(6)	N(2)-C(4)-C(5)-C(8)	-5.8(11)
O(2)-V(1)-N(2)-C(4)	-90.6(4)	O(1)-C(12)-C(13)-C(14)	-34.4(7)
O(2)-V(1)-N(2)-C(9)	84.0(6)	C(12)-C(13)-C(14)-C(15)	36.1(8)
N(1)-V(1)-N(2)-C(4)	1.0(3)	C(13)-C(14)-C(15)-O(1)	-24.4(8)
N(1)-V(1)-N(2)-C(9)	175.6(6)	O(2)-C(16)-C(17)-C(18)	33.5(9)
V(1)-O(1)-C(12)-C(13)	-164.7(4)	C(16)-C(17)-C(18)-C(19)	-24.(1)
C(15)-O(1)-C(12)-C(13)	19.6(8)	C(17)-C(18)-C(19)-O(2)	5.0(9)

[PhC(NSiMe$_3$)$_2$]$_2$V(η^3-C$_3$H$_5$) (**8**)			
N(2)-V-N(1)-Si(1)	170.24(12)	C(1)-Si(1)-N(1)-C(4)	-152.42(14)
N(2)-V-N(1)-C(4)	0.13(11)	C(2)-Si(1)-N(1)-V	-79.17(13)
N(3)-V-N(1)-Si(1)	-22.72(12)	C(2)-Si(1)-N(1)-C(4)	87.83(15)
N(3)-V-N(1)-C(4)	167.17(8)	C(3)-Si(1)-N(1)-V	159.59(10)
N(4)-V-N(1)-Si(1)	-90.85(11)	C(3)-Si(1)-N(1)-C(4)	-33.42(16)
N(4)-V-N(1)-C(4)	99.04(9)	C(11)-Si(2)-N(2)-V	87.38(14)
C(27)-V-N(1)-Si(1)	78.1(4)	C(11)-Si(2)-N(2)-C(4)	-73.88(16)
C(27)-V-N(1)-C(4)	-92.0(4)	C(12)-Si(2)-N(2)-V	-149.38(12)
C(28)-V-N(1)-Si(1)	101.97(14)	C(12)-Si(2)-N(2)-C(4)	49.36(16)
C(28)-V-N(1)-C(4)	-68.14(13)	C(13)-Si(2)-N(2)-V	-30.35(14)
C(29)-V-N(1)-Si(1)	101.5(4)	C(13)-Si(2)-N(2)-C(4)	168.40(14)
C(29)-V-N(1)-C(4)	-68.7(4)	C(14)-Si(3)-N(3)-V	93.04(15)
N(1)-V-N(2)-Si(2)	-165.53(13)	C(14)-Si(3)-N(3)-C(17)	-77.29(16)
N(1)-V-N(2)-C(4)	-0.13(9)	C(15)-Si(3)-N(3)-V	-144.68(13)
N(4)-V-N(2)-Si(2)	90.40(12)	C(15)-Si(3)-N(3)-C(17)	44.99(18)

N(4)-V-N(2)-C(4)	-104.20(9)	C(16)-Si(3)-N(3)-V	-24.89(16)
C(27)-V-N(2)-Si(2)	-73.0(4)	C(16)-Si(3)-N(3)-C(17)	164.78(15)
C(27)-V-N(2)-C(4)	92.4(4)	C(24)-Si(4)-N(4)-V	40.91(14)
C(28)-V-N(2)-Si(2)	-38.43(14)	C(24)-Si(4)-N(4)-C(17)	-145.60(16)
C(28)-V-N(2)-C(4)	126.97(12)	C(25)-Si(4)-N(4)-V	-79.48(14)
C(29)-V-N(2)-Si(2)	-9.0(2)	C(25)-Si(4)-N(4)-C(17)	94.02(17)
C(29)-V-N(2)-C(4)	156.44(19)	C(26)-Si(4)-N(4)-V	159.63(12)
N(1)-V-N(3)-Si(3)	86.23(13)	C(26)-Si(4)-N(4)-C(17)	-26.87(19)
N(1)-V-N(3)-C(17)	-101.29(10)	V-N(1)-C(4)-N(2)	-0.21(15)
N(4)-V-N(3)-Si(3)	-169.96(15)	V-N(1)-C(4)-C(5)	-179.80(13)
N(4)-V-N(3)-C(17)	2.52(9)	Si(1)-N(1)-C(4)-N(2)	-171.44(11)
C(27)-V-N(3)-Si(3)	-10.5(4)	Si(1)-N(1)-C(4)-C(5)	9.0(2)
C(27)-V-N(3)-C(17)	161.9(4)	V-N(2)-C(4)-N(1)	0.21(14)
C(28)-V-N(3)-Si(3)	-45.67(16)	V-N(2)-C(4)-C(5)	179.78(14)
C(28)-V-N(3)-C(17)	126.81(13)	Si(2)-N(2)-C(4)-N(1)	168.8(1)
C(29)-V-N(3)-Si(3)	-73.8(2)	Si(2)-N(2)-C(4)-C(5)	-11.6(2)
C(29)-V-N(3)-C(17)	98.69(19)	V-N(3)-C(17)-N(4)	-3.88(14)
N(1)-V-N(4)-Si(4)	-87.93(12)	V-N(3)-C(17)-C(18)	174.41(14)
N(1)-V-N(4)-C(17)	96.93(10)	Si(3)-N(3)-C(17)-N(4)	170.35(12)
N(2)-V-N(4)-Si(4)	-19.65(13)	Si(3)-N(3)-C(17)-C(18)	-11.4(2)
N(2)-V-N(4)-C(17)	165.21(9)	V-N(4)-C(17)-N(3)	4.09(15)
N(3)-V-N(4)-Si(4)	172.67(14)	V-N(4)-C(17)-C(18)	-174.21(14)
N(3)-V-N(4)-C(17)	-2.47(9)	Si(4)-N(4)-C(17)-N(3)	-171.44(12)
C(27)-V-N(4)-Si(4)	118.5(9)	Si(4)-N(4)-C(17)-C(18)	10.3(2)
C(27)-V-N(4)-C(17)	-56.6(9)	N(1)-C(4)-C(5)-C(6)	-86.82(19)
C(28)-V-N(4)-Si(4)	78.05(17)	N(1)-C(4)-C(5)-C(10)	91.62(19)
C(28)-V-N(4)-C(17)	-97.09(14)	N(2)-C(4)-C(5)-C(6)	93.62(19)
C(29)-V-N(4)-Si(4)	87.0(2)	N(2)-C(4)-C(5)-C(10)	-87.93(19)
C(29)-V-N(4)-C(17)	-88.13(19)	C(4)-C(5)-C(6)-C(7)	177.58(15)
N(1)-V-C(27)-C(28)	143.2(5)	C(10)-C(5)-C(6)-C(7)	-0.9(3)
N(2)-V-C(27)-C(28)	78.2(6)	C(4)-C(5)-C(10)-C(9)	-177.56(15)
N(3)-V-C(27)-C(28)	-109.6(5)	C(6)-C(5)-C(10)-C(9)	0.9(3)
N(4)-V-C(27)-C(28)	-61.7(12)	C(5)-C(6)-C(7)-C(8)	0.3(3)
C(29)-V-C(27)-C(28)	-26.3(4)	C(6)-C(7)-C(8)-C(9)	0.2(3)
N(1)-V-C(28)-C(27)	-44.2(7)	C(7)-C(8)-C(9)-C(10)	-0.2(3)
N(1)-V-C(28)-C(29)	-179.6(3)	C(8)-C(9)-C(10)-C(5)	-0.4(3)
N(2)-V-C(28)-C(27)	-101.6(7)	N(3)-C(17)-C(18)-C(19)	-94.3(2)
N(2)-V-C(28)-C(29)	123.0(3)	N(3)-C(17)-C(18)-C(23)	84.6(2)
N(3)-V-C(28)-C(27)	79.2(7)	N(4)-C(17)-C(18)-C(19)	83.9(2)
N(3)-V-C(28)-C(29)	-56.2(3)	N(4)-C(17)-C(18)-C(23)	-97.2(2)
N(4)-V-C(28)-C(27)	151.3(7)	C(17)-C(18)-C(19)-C(20)	178.37(16)
N(4)-V-C(28)-C(29)	15.9(3)	C(23)-C(18)-C(19)-C(20)	-0.5(3)
C(27)-V-C(28)-C(29)	-135.4(8)	C(17)-C(18)-C(23)-C(22)	-178.15(17)
C(29)-V-C(28)-C(27)	135.4(8)	C(19)-C(18)-C(23)-C(22)	0.7(3)
N(1)-V-C(29)-C(28)	0.8(6)	C(18)-C(19)-C(20)-C(21)	-0.3(3)
N(2)-V-C(29)-C(28)	-59.9(3)	C(19)-C(20)-C(21)-C(22)	0.8(3)
N(3)-V-C(29)-C(28)	128.1(3)	C(20)-C(21)-C(22)-C(23)	-0.6(3)
N(4)-V-C(29)-C(28)	-167.6(3)	C(21)-C(22)-C(23)-C(18)	-0.2(3)
C(27)-V-C(29)-C(28)	26.9(5)	V-C(27)-C(28)-C(29)	55.2(7)
C(1)-Si(1)-N(1)-V	40.59(13)	C(27)-C(28)-C(29)-V	-54.1(9)

[*t*-BuC(N*i*-Pr)$_2$]V(η^3-C_3H_5)$_2$ (**11**)

N(2)-V(1)-N(1)-C(1)	-168.2(2)	C(17)-V(1)-C(14)-C(13)	77.0(2)
N(2)-V(1)-N(1)-C(4)	-9.65(12)	N(1)-V(1)-C(15)-C(16)	-179.14(16)
C(12)-V(1)-N(1)-C(1)	36.2(2)	N(2)-V(1)-C(15)-C(16)	-112.56(17)

C(12)-V(1)-N(1)-C(4)	-165.24(14)	C(12)-V(1)-C(15)-C(16)	83.92(18)
C(13)-V(1)-N(1)-C(1)	65.1(2)	C(13)-V(1)-C(15)-C(16)	54.9(2)
C(13)-V(1)-N(1)-C(4)	-136.28(14)	C(14)-V(1)-C(15)-C(16)	44.1(3)
C(14)-V(1)-N(1)-C(1)	101.2(2)	C(17)-V(1)-C(15)-C(16)	-26.00(17)
C(14)-V(1)-N(1)-C(4)	-100.24(15)	N(1)-V(1)-C(16)-C(15)	1.2(2)
C(15)-V(1)-N(1)-C(1)	-55.1(2)	N(1)-V(1)-C(16)-C(17)	-134.5(2)
C(15)-V(1)-N(1)-C(4)	103.48(14)	N(2)-V(1)-C(16)-C(15)	87.98(19)
C(16)-V(1)-N(1)-C(1)	-55.8(3)	N(2)-V(1)-C(16)-C(17)	-47.7(3)
C(16)-V(1)-N(1)-C(4)	102.74(17)	C(12)-V(1)-C(16)-C(15)	-94.91(18)
C(17)-V(1)-N(1)-C(1)	-111.5(3)	C(12)-V(1)-C(16)-C(17)	129.4(2)
C(17)-V(1)-N(1)-C(4)	47.1(3)	C(13)-V(1)-C(16)-C(15)	-129.79(18)
N(1)-V(1)-N(2)-C(4)	9.39(12)	C(13)-V(1)-C(16)-C(17)	94.5(2)
N(1)-V(1)-N(2)-C(9)	-147.3(2)	C(14)-V(1)-C(16)-C(15)	-154.07(18)
C(12)-V(1)-N(2)-C(4)	64.6(2)	C(14)-V(1)-C(16)-C(17)	70.2(2)
C(12)-V(1)-N(2)-C(9)	-92.1(3)	C(15)-V(1)-C(16)-C(17)	-135.7(3)
C(13)-V(1)-N(2)-C(4)	115.35(16)	C(17)-V(1)-C(16)-C(15)	135.7(3)
C(13)-V(1)-N(2)-C(9)	-41.4(3)	N(1)-V(1)-C(17)-C(16)	91.9(3)
C(14)-V(1)-N(2)-C(4)	112.37(15)	N(2)-V(1)-C(17)-C(16)	141.5(2)
C(14)-V(1)-N(2)-C(9)	-44.3(2)	C(12)-V(1)-C(17)-C(16)	-54.1(2)
C(15)-V(1)-N(2)-C(4)	-80.76(15)	C(13)-V(1)-C(17)-C(16)	-85.1(2)
C(15)-V(1)-N(2)-C(9)	122.5(2)	C(14)-V(1)-C(17)-C(16)	-120.1(2)
C(16)-V(1)-N(2)-C(4)	-121.17(16)	C(15)-V(1)-C(17)-C(16)	27.0(2)
C(16)-V(1)-N(2)-C(9)	82.1(2)	V(1)-N(1)-C(1)-C(2)	30.1(3)
C(17)-V(1)-N(2)-C(4)	-146.19(15)	V(1)-N(1)-C(1)-C(3)	-92.3(2)
C(17)-V(1)-N(2)-C(9)	57.1(2)	C(4)-N(1)-C(1)-C(2)	-122.2(2)
N(1)-V(1)-C(12)-C(13)	131.86(18)	C(4)-N(1)-C(1)-C(3)	115.4(2)
N(2)-V(1)-C(12)-C(13)	83.6(3)	V(1)-N(1)-C(4)-N(2)	13.75(17)
C(14)-V(1)-C(12)-C(13)	28.89(19)	V(1)-N(1)-C(4)-C(5)	-159.82(19)
C(15)-V(1)-C(12)-C(13)	-127.23(19)	C(1)-N(1)-C(4)-N(2)	175.5(2)
C(16)-V(1)-C(12)-C(13)	-91.5(2)	C(1)-N(1)-C(4)-C(5)	2.0(3)
C(17)-V(1)-C(12)-C(13)	-64.1(2)	V(1)-N(2)-C(4)-N(1)	-14.37(18)
N(1)-V(1)-C(13)-C(12)	-57.2(2)	V(1)-N(2)-C(4)-C(5)	159.04(19)
N(1)-V(1)-C(13)-C(14)	75.2(2)	C(9)-N(2)-C(4)-N(1)	146.0(2)
N(2)-V(1)-C(13)-C(12)	-137.44(17)	C(9)-N(2)-C(4)-C(5)	-40.6(3)
N(2)-V(1)-C(13)-C(14)	-5.0(2)	V(1)-N(2)-C(9)-C(10)	92.1(3)
C(12)-V(1)-C(13)-C(14)	132.4(3)	V(1)-N(2)-C(9)-C(11)	-30.6(3)
C(14)-V(1)-C(13)-C(12)	-132.4(3)	C(4)-N(2)-C(9)-C(10)	-58.6(3)
C(15)-V(1)-C(13)-C(12)	58.0(2)	C(4)-N(2)-C(9)-C(11)	178.6(3)
C(15)-V(1)-C(13)-C(14)	-169.54(19)	N(1)-C(4)-C(5)-C(6)	61.6(3)
C(16)-V(1)-C(13)-C(12)	86.7(2)	N(1)-C(4)-C(5)-C(7)	-61.2(3)
C(16)-V(1)-C(13)-C(14)	-140.9(2)	N(1)-C(4)-C(5)-C(8)	178.3(2)
C(17)-V(1)-C(13)-C(12)	121.1(2)	N(2)-C(4)-C(5)-C(6)	-110.9(3)
C(17)-V(1)-C(13)-C(14)	-106.5(2)	N(2)-C(4)-C(5)-C(7)	126.3(2)
N(1)-V(1)-C(14)-C(13)	-118.54(18)	N(2)-C(4)-C(5)-C(8)	5.8(3)
N(2)-V(1)-C(14)-C(13)	176.29(18)	V(1)-C(12)-C(13)-C(14)	-56.0(3)
C(12)-V(1)-C(14)-C(13)	-27.96(18)	C(12)-C(13)-C(14)-V(1)	58.1(3)
C(15)-V(1)-C(14)-C(13)	17.4(3)	V(1)-C(15)-C(16)-C(17)	54.1(3)
C(16)-V(1)-C(14)-C(13)	44.2(2)	C(15)-C(16)-C(17)-V(1)	-51.3(3)

The sign of the torsion angle is positive if when looking from atom-2 to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.

References.

1. Bolhuis, F. van *J. Appl. Cryst.* **1971**, *4*, 263-264.
2. Enraf-Nonius *CAD4-UNIX* Version 5.1, Utrecht modified version October 1994. Enraf-Nonius Delft, Scientific Instruments Division, Delft, The Netherlands.
3. Duisenberg, A. J. M. *J. Appl. Cryst.* **1992**, *25*, 92-96.
4. Boer, J. L. de & Duisenberg, A. J. M. *Acta. Cryst.* **1984**, *A40*, C410.
5. Spek, A.L. *J. Appl. Cryst.* **1988**, *21*, 578-579.
6. Le Page, Y. *J. Appl. Cryst.* **1987**, *20*, 264-269.
7. Le Page, Y. *J. Appl. Cryst.* **1988**, *21*, 983-984.
8. Spek, A.L. *HELENA. Program for Reduction of CAD4 Data.*, Utrecht Univ., The Netherlands, **1993**.
9. Beurskens, P.T., Beurskens, G., Bosman, W.P., Gelder, R. de, García-Granda, S., Gould, R.O., Israël, R. & Smits, J.M.M. The *DIRDIF-97* program system, Crystallography Laboratory, University of Nijmegen, The Netherlands, **1997**.
10. *International Tables for Crystallography* **1992**, Vol. C. Edited by A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht, The Netherlands.
11. Sheldrick, G.M. *SHELX-97. Program for the Solution and Refinement of Crystal Structures*. Univ. of Göttingen, Germany, **1997**.
12. Spek, A.L. *PLATON. Program for the Automated Analysis of Molecular Geometry.* Version of October **1996**, Univ. of Utrecht, The Netherlands.
13. Meetsma, A. *PLUTO. Program for the Display and Analysis of Crystal and Molecular Structures.* Version of October **1996**, Univ. of Groningen, The Netherlands.
14. Hall, S.R, Allen, F.H. & Brown, I.D. *Acta Cryst.* **1991**, *A47*, 655-685.
15. Burnett, M.N. & Johnson, C.K. *ORTEPIII.* Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA, **1996**.
16. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441-451.
17. Spek, A.L. *Acta Cryst.* **1990**, *A46*, C-34.
18. Spek, A.L. *Am. Crystallogr. Assoc. Abstr.* **1994**, **22**, 66.
19. *International Tables for Crystallography* **1983**, *Vol. A.* Space-group symmetry, edited by T. Hahn. Dordrecht: Reidel. (Present distributor Kluwer Academic Publishers, Dordrecht).
20. Fisher, R.X. & Tillmanns, E. *Acta Cryst.* **1988**, *C44*, 775-776.

Figure 1. ORTEP drawing of [*t*-BuC(N*i*-Pr)$_2$]VCl$_2$(THF)$_2$ (**5**)

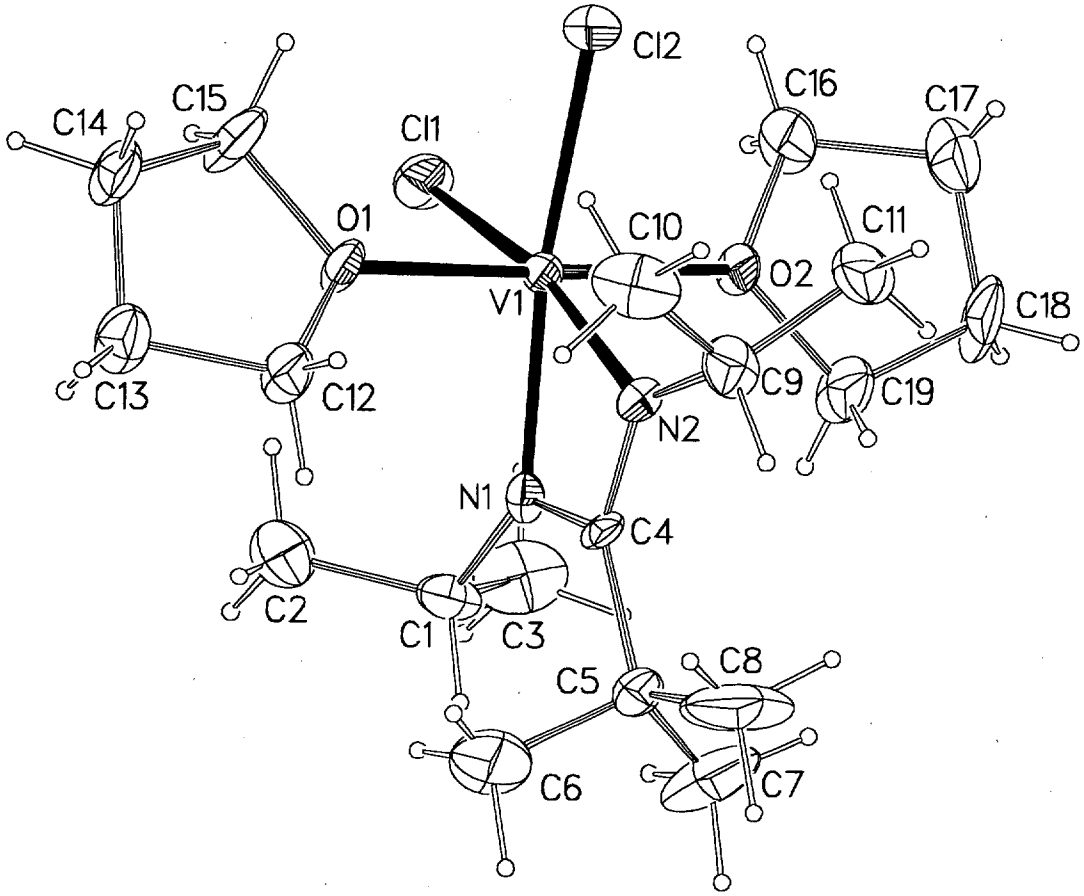

Figure 2. ORTEP drawing of $[PhC(NSiMe_3)_2]_2V(\eta^3\text{-}C_3H_5)$ (**8**)

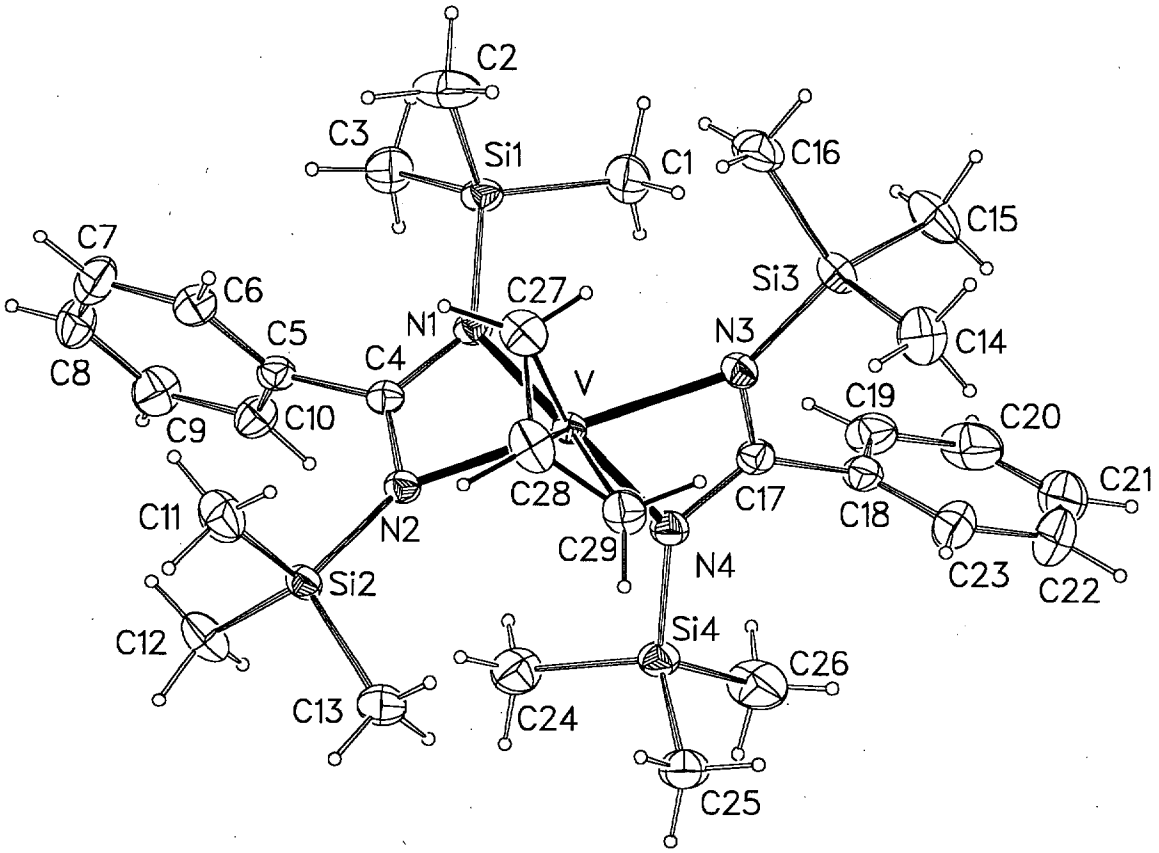

Figure 3. ORTEP drawing of [*t*-BuC(N*i*-Pr)$_2$]V(η^3-C_3H_5)$_2$ (**11**)